A Recyclable Metal-Organic Framework as a Dual Detector and Adsorbent for Ammonia

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Abstract: *Recyclable materials for simultaneous detection and uptake of ammonia (NH_3) are of great interest due to the hazardous nature of NH_3. The structural versatility and porous nature of metal-organic frameworks (MOFs) make them ideal candidates for NH_3 capture. Herein, we report the synthesis of a water-stable and porous 3-dimensional Cu(II)-based MOF (**SION-10**) displaying a ship-in-a-bottle structure; the pores of the host **SION-10** framework accommodate mononuclear Cu(II)-complexes. **SION-10** spontaneously uptakes NH_3 as a result of two concurrent mechanisms: chemisorption due to the presence of active Cu(II) sites and physisorption (bulk permanent porosity). The color of the material changes from green to blue upon NH_3 capture, with the shifts of the absorption bands clearly seen at NH_3 concentrations as low as 300 ppm. **SION-10** can be recovered upon immersion of **SION-10⊃NH$_3$** in liquid water and can be further reused for NH_3 capture for at least three cycles.*

Ammonia (NH_3) is a corrosive and toxic gas with a strong odor that is widely produced and used in industries. In industrial settings, 25 ppm of NH_3 is the exposure limit recommended by the US Occupational Safety and Health Administration,[1] and exposure to up to 300 ppm of NH_3 can cause serious health issues.[2] Meanwhile, there is still a very high demand for NH_3 at the industrial scale as reflected by its production of 145 million tons in 2014.[3] NH_3 is an important raw material for the manufacturing of large numbers of chemicals including fertilizers, dyes, plastics, and pharmaceuticals,[4] and is considered as a potential carbon-free green fuel due to its high energy density and its lower cost of production, storage, and delivery compared to hydrogen.[5] Both the danger and usefulness of NH_3 have motivated researchers to develop economical and responsive materials that can selectively detect and capture NH_3; for example, NH_3 sensors based on catalytic metals[6] and conducting polymers[7] have been reported, whilst porous materials such as activated carbons,[8] organic polymers,[9] covalent organic frameworks,[10] and MOFs[11] are known as efficient NH_3 sorbents.

MOFs are crystalline materials prepared by the self-assembly of metal ions or clusters with organic ligands to form porous extended structures.[12] MOFs are characterized by high porosity, with some of them possessing the highest volume and surface area, and lowest crystal density among all materials known to date.[13] The immense choice of metal ions or clusters and ligands offers vast opportunities to rationally design and synthesize MOFs with specific functionalities for targeted applications in areas of gas storage and separation,[14] catalysis,[15] sensing,[16] non-linear optics,[17] ferroelectricity,[18] magnetism,[19] and conductivity.[20] Recently, there is an increasing interest in developing porous and robust MOFs for the selective detection, capture and destruction of harmful molecules including toxic industrial chemicals (SO_2 and NH_3), and chemical warfare agents (sarin, sulfur mustard, and dimethyl methylphosphonate).[21]

Due to the high basicity and corrosivity of NH_3, the most challenging task in the MOF research area is to develop sorbents and detectors that can efficiently capture and detect NH_3, and can be recycled while retaining their structural integrity.[22] Recently, Dincă *et al.* have reported mesoporous and robust azolate-based MOFs exhibiting open Mn(II), Co(II), and Ni(II) sites which display high and reversible NH_3 uptake.[11] The strategy of employing azolates to increase the stability of MOFs, initially addressed by Rosi *et al.*,[23] motivated us to synthesize **SION-10** by employing adenine in the MOF structure. We chose to use Cu(II) in which, along with other d-element cations in MOFs, has the potential to introduce strong interactions with NH_3.[22, 24] **SION-10** is a 3-dimensional MOF based on the earth abundant Cu(II) and readily available benzene-1,3,5-tricarboxylic acid and adenine ligands. It exhibits reversible NH_3 uptake, and displays a visible and reversible color change upon adsorption and desorption of NH_3.

SION-10 was synthesized hydrothermally after mixing $CuCO_3$ with 1,3,5-benzenetricarboxylic acid (H_3btc) and adenine (9Hade) (see SI Section 1 for the synthesis details) in pure water for 48 hours at 100 °C. The crystals obtained were characterized by single-crystal X-ray diffraction (SCXRD). **SION-10** with the formula of $[Cu_4(btc)_2(ade)(1Hade)(\mu_3\text{-}OH)(H_2O)_3]\cdot 0.4[Cu(ade)_2(H_2O)_4]\cdot 10.5(H_2O)$ crystallizes in the triclinic space group $P\bar{1}$ (SI Section 3), and comprises three components: *i.* a 3-dimensional host framework - $[Cu_4(btc)_2(ade)(1Hade)(\mu_3\text{-}OH)(H_2O)_3]$, *ii.* guest mononuclear complexes that are partially occupying the void channels within the host **SION-10** - $0.4[Cu(ade)_2(H_2O)_4]$ (Figure 1), and *iii.* highly disordered guest H_2O solvent molecules. The host framework of **SION-10** is based on Cu-paddlewheel units, in which two Cu1

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atoms are bridged by two deprotonated ade$^-$ ligands *via* an $\eta^1:\eta^1$ binding mode through their N3 and N9 atoms (ade$^-$ colored in green – Figure 1a). The neutral 1Hade ligand is coordinated *via* N7 to the axial sites of the Cu-paddlewheel (1Hade colored in orange – Figure 1a). The coordination of the paddlewheel is completed by the two bridging carboxylates from two crystallographically equivalent btc^{3-} ligands. The Cu-paddlewheel units are connected to each other *via* a tetranuclear Cu-cluster, $Cu_4(\mu_3\text{-}OH)_2$ (Figure 1b), constructed from four Cu(II) centers (two Cu2 and two Cu3) linked by two μ_3-hydroxo groups.[25] All Cu2 and Cu3 display a square pyramidal coordination geometry. The apical positions of these pyramids are occupied by H_2O molecules coordinated to Cu(II) through considerably long bonds (Cu2–O2 2.431(6) Å, Cu3–O3 2.424(6) Å). A single Cu4 atom, also with a square pyramidal coordination geometry, bonds to two btc^{3-} ligands (monodentate – yellow and bidentate – pink), one ade$^-$ and one H_2O molecule (Cu4–O4 2.211(0) Å - Figure 1c), and acts as a link between Cu-paddlewheel units and tetranuclear Cu-clusters. The host framework of **SION-10** displays an accessible volume of 37.9%, as determined by PLATON.[26]

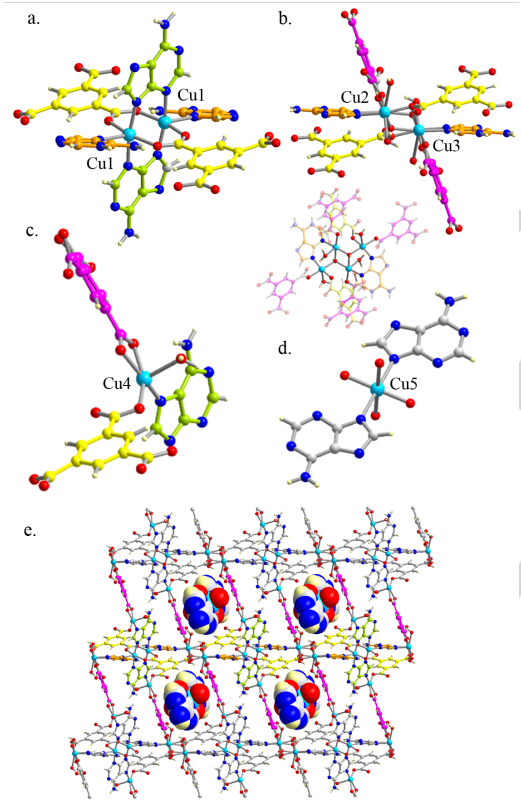

Figure 1. The structure of **SION-10** consists of: a. Cu1-paddlewheel units which are linked to b. Cu2Cu3 tetranuclear clusters $Cu_4(\mu_3\text{-}OH)_2$ and c. mononuclear Cu4 to extend the structure in 3-dimensions. d and e. The pores of the host **SION-10** accommodate guest mononuclear Cu5-complexes generating a material with ship-in-a-bottle structure. Atom color code: C gray, H pale yellow, N blue, O red, Cu cyan.

The cavities of the host **SION-10** framework are occupied by mononuclear complexes with the formula of $[Cu(ade)_2(H_2O)_4]$ present with 80% partial occupancy (Figures 1d, and S3). The octahedrally coordinated Cu5 of the complex displays a Jahn–Teller distortion with two long Cu–N(ade) bonds (2.226(17) Å), two long Cu–OH_2 bonds (2.24(2) Å), and two short Cu–OH_2 bonds (1.941(14) Å) (Figure 1d). The complex displays π–π stacking interactions between the pyrimidine ring of the ade$^-$ group and the phenyl ring of the btc^{3-} ligand with a distance of about 3.7 Å (Figure S4), and is involved in an array of hydrogen bonds that stabilize its position within the framework cavities (Figure S5). Our attempts to wash the Cu(II)-complexes out were not successful, confirming that they cannot be removed from the host **SION-10** framework. Interestingly, molecular crystals of $Cu(ade)_2(H_2O)_4$ are not known, and the theoretically predicted structure of this complex[27] is markedly different from the one reported in this work. Thus, **SION-10** represents a typical example of a ship-in-a-bottle material. It is worth noting here that although the encapsulation of molecular species in the pores of a MOF is known,[28] the direct observation of them as a part of a refined crystal structure is rather rare.[29] The accessible volume of **SION-10** (with the complexes present within the channels) was found to be 20.3%,[26] revealing that the complexes occupy nearly half of the accessible volume of the host-framework voids.

The phase purity of **SION-10** was confirmed by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and elemental analysis (EA), whereas the thermogravimetric (TGA) profile coupled with the variable-temperature (VT) PXRD study revealed the thermal stability of **SION-10**. The PXRD pattern of **SION-10** (Figure 2a) can be indexed to unit-cell parameters consistent with the parameters obtained from SCXRD (SI Section 5a). SEM images reveal only one type of crystal morphology (Figure S14). Elemental and inductively coupled plasma (ICP) analyses confirmed that the $[Cu(ade)_2(H_2O)_4]$ complex is not 100% present within the pores as the composition of **SION-10** can fit to the formula derived from the SCXRD data (SI Section 5c). FTIR spectra show characteristic features originating from both

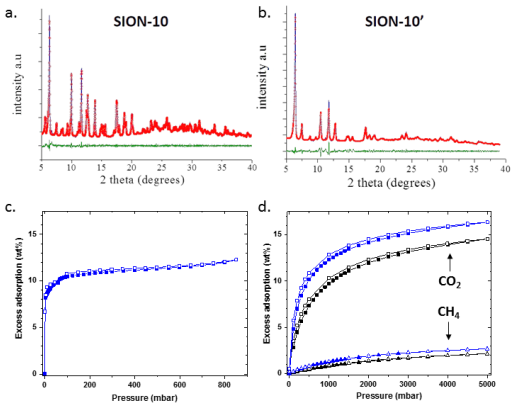

Figure 2. Le Bail fits of a. **SION-10** and b. **SION-10'** collected at 298 K using the Cu K_α. The blue plots represent the experimental data, the red dots show the refined Le Bail profiles while the green plots represent the difference between them. **SION-10'** is porous to: c. N_2 at 77 K and 900 mbar and d. CO_2

(top two plots) and CH_4 (bottom two plots) at 273 (blue plots) and 298 K (black plots) and 5000 mbar. In c. and d. full symbols represent adsorption, while the empty ones show the desorption.

ligands present in the structure of **SION-10** (Figure S11). The TGA profile of **SION-10** shows that the coordinated and guest H_2O molecules can be removed in the temperature range of 30–265 °C with the total loss of 20.8% (Figure S9). The weight loss observed in TGA is in good agreement with the weight loss calculated from the EA (20.0%). Above 250 °C a substantial decrease in crystallinity is observed from the VT PXRD study (Figure S6) and the decomposition of **SION-10** starts at 295 °C. As confirmed by PXRD (Figure S8) **SION-10** is stable in liquid water as well as in acidic and basic aqueous solutions, thus confirming its hydrolytic stability.

The activated **SION-10′** was generated by heating the as-synthesized **SION-10** at 120 °C under vacuum (10^{-6} mbar). The weight loss of 19.8 % is consistent with the weight loss observed by TGA and EA. The PXRD pattern of **SION-10′** (Figure 2b) shows the retention of crystallinity and Le Bail fits revealed that the unit cell is contracted by 3.5% compared to the cell parameters of **SION-10** (SI Section 5a). When **SION-10′** is exposed to the atmosphere for 1-2 hours or is immersed in liquid H_2O (10 mins), **SION-10** can be recovered. This suggests that **SION-10′** with open Cu(II) sites has high affinity for H_2O, and thus the re-coordination of H_2O molecules to Cu(II) leads in the generation of the ordered **SION-10** structure.

SION-10′ is permanently porous to N_2 at 77 K and 1 bar, exhibiting a reversible type I sorption behavior characteristic for microporous materials (Figure 2c). Application of the Brunauer–Emmett–Teller (BET) model in the relative pressure p/p^0 range of 0.02–0.22 results in a surface area of ~300 m^2/g. The calculated pore volume of **SION-10′** is 0.138 cm^3/g, which is in good agreement with the pore volume derived from the single crystal data of the static structure of **SION-10** (0.132 cm^3/g). **SION-10′** is porous to CO_2 and CH_4 at 273 and 298 K (type I isotherms, Figure 2d) and the isosteric heats of adsorption Q_{st} at zero coverage derived from the virial-type expression are 30.8 kJ/mol for CO_2 and 21.3 kJ/mol for CH_4.

Since the complexes do not block the porosity in **SION-10′** where open Cu(II) are present, and both polar and non-polar molecules can diffuse in the accessible voids, we subjected **SION-10′** to NH_3 adsorption, with the NH_3 vapor generated by evaporation of a 25% ammonia solution at room temperature. Upon exposing the green powder of **SION-10′** to NH_3 vapor, a color change was immediately noticed and the green color changed to blue, whilst its shade deepened over a loading period of 30 mins (Figure 3c, inset). The formula of **SION-10⊃NH$_3$** (30 mins loading) corresponds to $[Cu_4(btc)_2(ade)(1Hade)(\mu_3\text{-}OH)(NH_3)_3]\cdot 0.4[Cu(ade)_2(NH_3)_4]\cdot 4(NH_3)\cdot 6.5(H_2O)$, revealing that the amount of chemisorbed NH_3 was 6.37 mmol/g (SI Section 5c and Figure S10). NH_3 molecules displace all H_2O ligands previously coordinated to Cu(II), and a part of non-coordinated H_2O guest molecules. In order to further evaluate the capability of **SION-10′** to selectively capture NH_3, we have performed a breakthrough experiment using a 10mL min^{-1} flow of N_2/NH_3 (9:1) gas mixture at 303 K (Figure 3a). At the NH_3 partial pressure of 0.1 bar **SION-10′** exhibited the adsorption capacity of 27.3 mmol/g. In a separate experiment, the adsorption capacity of **SION-10′** at the N_2 partial pressure of 0.9 bar and at 303 K was investigated (Figure S13). The amount of N_2 adsorbed (0.170 mmol/g) was significantly lower than that of NH_3, resulting in a NH_3/N_2 selectivity factor of 1440. This result is indicative of a selective and strong interaction of NH_3 molecules with **SION-10′** due to chemisorption (presence of active Cu(II) centers) and physisorption (narrow pores of **SION-10′**), and places **SION-10′** among materials with the highest NH_3 capacity reported up to date.[9, 11]

Interestingly, the color change experienced by the NH_3 loaded **SION-10′** was also observed when the as-made **SION-10** was exposed to NH_3 vapors. The immersion of the blue **SION-10⊃NH$_3$** in liquid water resulted in the isolation of a green material suggesting that **SION-10** could potentially be recovered. The PXRD patterns show that although the crystallinity of **SION-10⊃NH$_3$** is reduced to a significant degree, the recovered material displays the same pattern as with **SION-10**, confirming the regeneration of **SION-10** (Figure S7). The FTIR spectrum of **SION-10⊃NH$_3$** (Figure 3b) shows a nearly identical pattern with that of **SION-10** with characteristic bands at 3400–3300 cm^{-1}

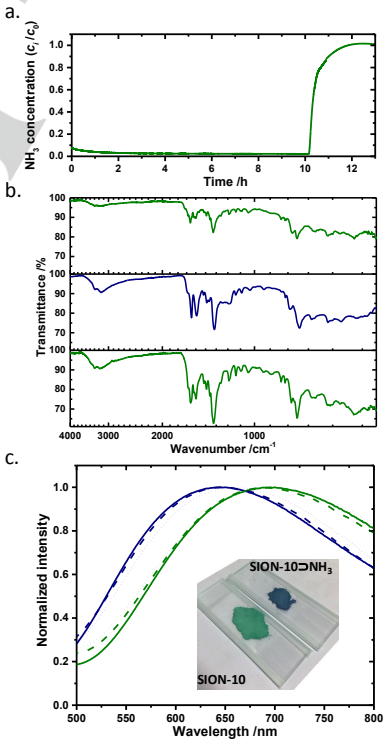

Figure 3. a. Breakthrough profile of N_2/NH_3 (9:1) gas mixture at 303 K over **SION-10′**. b. FTIR spectra of the as-made **SION-10** (top), **SION-10⊃NH$_3$** (middle) and recovered **SION-10** (bottom) upon immersion of **SION-10⊃NH$_3$** in liquid H_2O, c. UV/Vis spectra of **SION-10** (green plots) and **SION-10⊃NH$_3$** (blue plots) and cycling NH_3 adsorption/desorption (first, second, and third uptake/regeneration cycles are shown in solid, dash, and dot lines, respectively). Inset: a photograph showing the color difference between **SION-10** and **SION-10⊃NH$_3$**.

and 1640 cm^{-1}, corresponding to the N–H, O–H, and C=O stretching bands of the ade^{-}, the OH^{-} bridge/H_2O molecule, and the C=O of the btc^{3-} ligand, suggesting that despite the low crystallinity it has the same structural fingerprint as **SION-10**. To further investigate the impact of NH_3 uptake by **SION-10** and its regeneration, the UV/Vis diffuse reflectance spectra were collected (Figure 3c). The UV/Vis spectra revealed a blue-shift of ~70 nm of the Cu(II) *d*–*d* transition band of **SION-10⊃NH$_3$** compared to **SION-10**, suggesting the formation of new Cu–NH_3 bonds that are formed after the stronger-field NH_3 ligands substitute the weak-field H_2O ligands bound to Cu(II) centers. The recovered **SION-10** displayed a comparable absorption band compared to the pristine **SION-10**, indicating that **SION-10** could be recycled, and we successfully performed three NH_3 adsorption-desorption NH_3 cycles (Figure 3c). Previous studies demonstrated that the presence of open metal sites within MOFs are key factors for the capture of NH_3. However, MOFs endowed with open metal sites were shown to reduce their porosity and crystallinity to a considerable extent when loaded with NH_3 vapors.[22] For **SION-10**, we strongly believe that the combination of narrow pores generated from the presence of the complexes, and the presence of active Cu(II) sites are the key factors for the efficient capture of NH_3.

The substantial green-to-blue color change was not observed with other gases (such as CO_2, N_2 and CH_4) suggesting that **SION-10** can also act as a selective detector for NH_3 vapor. When 5 mg of **SION-10** were exposed to controlled atmospheres of NH_3 with concentrations of 300 and 600 ppm, the shifts of the absorption bands were clearly observed (Figure S12), indicating the relatively high sensitivity of **SION-10** toward NH_3. In addition, the fast response time, i.e. immediate color changes, ensures that **SION-10** can quickly detect the presence of NH_3 in the atmosphere. The high thermal and hydrolytic stability together with the uptake of NH_3, and its recyclability confirm that **SION-10** can be potentially used as a dual detector and adsorbent for NH_3.

In conclusion, we report the synthesis of a ship-in-a-bottle **SION-10** material that is stable in water, and upon activation it is porous to N_2, CO_2 and CH_4. The presence of the mononuclear Cu(II) complexes decorate the pores of the host **SION-10′** with active Cu(II) sites that allow NH_3 to be chemisorbed. **SION-10′** adsorbs up to a paramount value of 27.3 mmol of NH_3 per gram (chemisorption and physisorption) which is one of the highest NH_3 uptake reported to date. The high sensitivity and selectivity of **SION-10** toward NH_3 makes **SION-10** the first MOF that can quickly uptake NH_3, easily regenerated and reused. In addition, it can detect NH_3 at concentrations as low as 300 ppm.

This work demonstrates a step forward toward the discovery of versatile, easily prepared and recyclable MOFs acting as dual detectors and adsorbents for NH_3 and further synthetic efforts in developing novel porous and water stable MOFs sensitive to NH_3 concentrations lower than 300 ppm are in progress.

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Keywords: metal-organic framework • ammonia • recyclability • ship-in-a-bottle • capture • detection

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[25] The presence of the μ_3-OH groups was confirmed by the bond valence sum calculation: $s = \text{sum}(s_{ij}) = \text{sum}[\exp(R_{ij}-d_{ij})/b]$, where R_{ij} = 1.649 for Cu(II)-O, d_{ij} is the Cu(II)-O bond distances, b = 0.37. The value obtained was 1.23. For O, a value of 0-0.4 indicates H_2O, 1-1.4 indicates OH, and 1.8-2.2 indicates O^{2-}.

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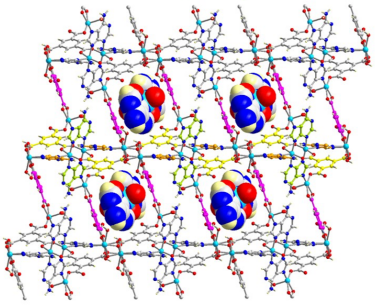
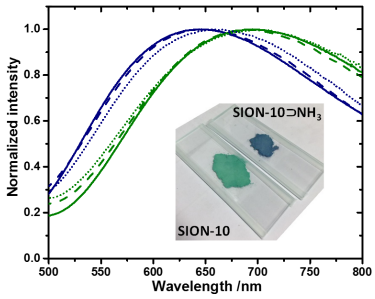
Entry for the Table of Contents

COMMUNICATION





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A Recyclable Metal-Organic Framework as a Dual Detector and Adsorbent for Ammonia

Response to Ammonia. SION-10, a water stable and porous ship-in-a-bottle structure, uptakes NH_3 spontaneously and displays high sensitivity toward this hazardous gas. The **SION-10⊃NH_3** can be easily regenerated and recycled for at least three times.